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(54)【発明の名称】 全固体二次電池

(57)【要約】

【目的】 高電圧、大容量でかつ、充放電特性、安全性に優れた全固体二次電池を提供する。

【構成】 負極、高分子固体電解質、正極からなる全固体二次電池において、高分子固体電解質が、高分子マトリクスと金属塩電解液を主成分とし、水、極性溶媒又は両者の混合物に可溶な高分子、界面活性剤又は両者の混合物を含むものであり、かつ高分子マトリクスと金属塩電解液が相分離し、前記の高分子、界面活性剤又は両者の混合物が高分子マトリクスと金属塩電解液の相互分散を安定させていること、並びに前記正極が電池正極活物質微粒子及び電子伝導体を該高分子電解質中に分散した正極シートである全固体二次電池。

【効果】 全固体二次電池の特性向上を達成できる利点がある。

【特許請求の範囲】

【請求項1】 負極、高分子固体電解質、正極からなる全固体二次電池において、前記高分子固体電解質が、高分子マトリクスと金属塩電解液を主成分とし、水、極性溶媒又は両者の混合物に可溶な高分子、界面活性剤又は両者の混合物を含むものであり、かつ高分子マトリクスと金属塩電解液が相分離し、前記の水、極性溶媒又は両者の混合物に可溶な高分子、界面活性剤又は両者の混合物が高分子マトリクスと金属塩電解液の相互分散を安定させていること、並びに前記正極が電池正極活物質微粒子及び電子伝導体を該高分子電解質中に分散した正極シートであることを特徴とする全固体二次電池。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、特に、リチウム固体二次電池などの高エネルギー密度固体二次電池に関する。詳細には高電圧、大容量でかつ、充放電特性、安全性に優れた全固体二次電池に関する。

【0002】

【従来の技術】近年、小型、携帯電子機器用の電源として、高エネルギー密度を有する電池のニーズが高まっている。このようなニーズを満たす電池の代表的なものとして、アルカリ金属、特にリチウムを負極に使った電池が挙げられる。現在リチウム電池は、電解質にリチウム塩を溶解した有機電解液を用いているため、液漏れ、デンドライトショートなど、安全面での信頼性が十分とはいえない。このため無機物や高分子でできた固体電解質を用いた、全固体型の電池の実現が期待されている。中でも電解質に高分子固体電解質を、また正極にイオン伝導性のある高分子固体電解質をバインダーとする正極シートを用いて構成される固体電池は、大面積化が容易で大容量の電池が実現可能であることや、作製法が比較的簡易であることから、近年盛んに検討が進められている。このような高分子固体電解質には従来、ポリエチレンオキシド(PEO)等のポリエーテル化合物中に金属塩を溶解させた系が盛んに研究されてきたが(例えば、渡辺、緒方、金属表面技術、第37巻、第5号、第214～221頁(1986)参照)、室温付近において 10^{-3} S/cm以上のイオン伝導率を発現することは不可能であった。また近年、極性高分子に金属塩電解質溶液を含浸させた電解液含浸型の高分子固体電解質が注目を浴び(例えば、コックスバン(Koksbanq)ほか、ジャーナル オブ パワーソース(Journal of Power Sources)、第32巻、第175～185頁(1990)参照)、そのイオン伝導率は 10^{-3} S/cm台に達しているが、放射線照射等の危険で、コストのかかる工程を経るなど製造工程に問題点を有していた。一方、従来の正極シートの研究例として、PEOに金属塩を溶解した高分子固体電解質をバインダーに用いた例(例えば、M. Z. A. ムンシ(M. Z. A. Munshi)ほか、ソリッド

ステート アイオニクス(Solid State Ionics)、第41巻、第41～46頁(1988))があるが、PEOが軟化する60℃以上では良好な特性を示すものの、室温付近においては、正極シート中のイオン拡散が遅く、更に正極活物質と高分子固体電解質との界面の接触が悪く、正極の利用率が低くなるという欠点を有していた。

【0003】

【発明が解決しようとする課題】本発明はこのような現状にかんがみてなされたものであり、その目的は、高電圧、大容量でかつ、充放電特性、安全性に優れた全固体二次電池を提供することにある。

【0004】

【課題を解決するための手段】本発明を概説すれば、負極、高分子固体電解質、正極からなる全固体二次電池に関する発明であって、前記高分子固体電解質が、高分子マトリクスと金属塩電解液を主成分とし、水、極性溶媒又は両者の混合物に可溶な高分子、界面活性剤又は両者の混合物を含むものであり、かつ高分子マトリクスと金属塩電解液が相分離し、前記の水、極性溶媒又は両者の混合物に可溶な高分子、界面活性剤又は両者の混合物が高分子マトリクスと金属塩電解液の相互分散を安定させていること、並びに前記正極が電池正極活物質微粒子及び電子伝導体を該高分子電解質中に分散した正極シートであることを特徴とする。

【0005】本発明の固体二次電池に用いられる負極は、例えばリチウム二次電池への適用を考えた場合、リチウム金属箔、リチウム-アルミニウム合金、あるいはリチウム-炭素等の低電位層間化合物が好適に用いられる。

【0006】本発明の固体二次電池に用いられる高分子固体電解質は、高分子微粒子分散液から作製されたマトリクスフィルム中に金属塩電解液からなるイオン伝導路が形成されている。この高分子固体電解質は高分子マトリクス中の極性安定剤(分散媒体に可溶な高分子、界面活性剤又は両者の混合物)の凝集部分に電解液を含浸させて製造できる。あるいはまた、高分子微粒子分散液にあらかじめ金属塩を溶解し、高分子マトリクスを形成後、作製された高分子マトリクスフィルム中の極性安定剤と金属塩の凝集部分に、金属塩を溶解する極性溶媒、水又は両者の混合物を含浸させて、金属塩を溶解した電解液からなるイオン伝導路を形成することができる。これらの高分子固体電解質では電解液が高分子マトリクスから相分離しているため、高分子マトリクス中に電解液が分子レベルで分散している従来の電解液含浸型高分子固体電解質と異なり、電解液と高分子マトリクスの静電的な相互作用がある場合のイオン移動の阻害が抑えられ、長期使用に対しても安定で、かつ高イオン伝導性のイオン伝導路が得られる。

【0007】また、極性の電解液と相分離させるために

は、高分子マトリクスは極性が低いことが必要で、例えば安価な炭化水素系高分子又はその共重合体が好適に用いられる。更に、この高分子固体電解質は、製造プロセスが単純なため、低い製造コストが期待できる。

【0008】この高分子固体電解質を製造するときに使用する高分子微粒子の成分としては、高分子マトリクスを形成したときの高分子成分が電解液と相分離するものであればどのようなものでもよいが、極性が低い高分子、例えば、安価な炭化水素系高分子又はその共重合体を成分とするものが好適である。高分子微粒子中の高分子成分としては、例えば、次のようなものの単独あるいは混合物が挙げられる：ポリスチレン、ポリプロピレン、ポリイソブテン、ポリエチレン、ポリブタジエン、ポリイソプレン、ポリ(α-メチルスチレン)、ポリブチルメタクリレート、ポリブチルアクリレート、ポリ(2-エチルヘキシルアクリレート)、ポリジブチルフタレート、ポリビニルブチルエーテル、ポリビニルブチラール、ポリビニルホルマール及びこれらの成分を含む共重合体等。高分子微粒子についても、異なる成分を持つ複数種の微粒子の混合でも良い。微粒子の高分子微粒子の粒径は、0.01~50 μmのものが好適に用いられる。

【0009】高分子微粒子分散液の安定剤には、界面活性剤が好適に使われ、例えば、次のようなものが挙げられる：脂肪酸金属塩、アルキルベンゼンスルホン酸金属塩、アルキル硫酸金属塩、ジオクチルスルホコハク酸金属塩、ポリオキシエチレノールフェニルエーテル、ポリオキシエチレンステアリン酸エステル、ポリオキシエチレンソルビタンモノラウリン酸エステル、ポリオキシエチレン-ポリオキシプロピレンブロック共重合体、ポリエーテル変性シリコンオイル等の単独あるいは混合物。

【0010】また、安定剤として分散媒体に溶解可能な高分子等を使用して、高分子微粒子を分散させても良い。このような高分子としては、分散媒体によって異なるが、水が分散媒体の場合、ヒドロキシエチルセルロース、ポリビニルアルコール、ポリアクリル酸金属塩、メチルセルロースなどが挙げられる。高分子微粒子分散液の分散媒体には、水が好適に用いられるが、アルコール類など極性有機溶媒を使用することができる。

【0011】イオン伝導路となる電解液の構成要素である金属塩は、作製する高分子電解質の用途によって異なるが、例としてリチウム電池への適用を考えると、LiClO₄、LiAlCl₄、LiBF₄、LiPF₆、LiAsF₆、LiNbF₆、LiSCN、LiCl、Li(CF₃SO₃)、Li(C₂H₅SO₃)等のリチウム塩及びこれらの混合物が例として挙げられる。

【0012】また、同様に例としてリチウム電池への適用を想定すると、電解液の溶媒には、プロピレンカーボネート、エチレンカーボネート、γ-ブチロラクトン、

ジメチルカーボネート、ジメチルスルホキシド、アセトニトリル、スルホラン、ジメチルホルムアミド、ジメチルアセトアミド、1,2-ジエトキシエタン、1,2-ジメトキシエタン、テトラヒドロフラン、2-メチルテトラヒドロフラン、ジオキソラン、メチルアセテート等の非プロトン性極性溶媒及びこれらの混合物が例として挙げられる。上記金属塩と溶媒の混合比は、高分子固体電解質中に形成されたイオン伝導路で、金属塩濃度が0.01~5 mol/lとなるように調製することが好適である。

【0013】高分子微粒子分散液は、高分子溶液を分散溶媒中に展開・分散させて微粒子化し、界面活性剤又は分散媒体に可溶性の高分子を用いて安定化させて製造することができるが、水系分散媒体中で乳化重合法で製造するのが好適である。また、高分子微粒子分散液は、アルコールなどの極性溶媒中、分散重合で製造することもできる〔例えば、Y. アルモグ (Y. Almq) はか、ブリティッシュ ポリマー ジャーナル (British Polymer Journal)、第14巻、第131頁 (1982) 参照〕。乳化重合法による高分子分散液の製法は一般的によく知られているものでよく〔例えば、室井宗一著、高分子ラテックス入門 (初版第1刷) (工文社、昭和55年7月29日発行) 参照〕、以下に概説する。水中に界面活性剤を臨界ミセル濃度以上に加え、モノマーを導入すると、モノマーの一部は界面活性剤ミセル内部に取込まれる。水溶性の重合開始剤を加え、加熱すると重合開始剤ラジカルが発生し、これがモノマーで膨潤したミセルに入り込むと、モノマーが重合して高分子が合成される。重合反応により高分子微粒子が成長する間、モノマーは乳化されたモノマー滴から水中溶解を経て、反応場のミセルに供給される。高分子微粒子の径は、反応時間を調整することにより制御できる。

【0014】高分子固体電解質の高分子マトリクスフィルムは、高分子微粒子分散液から水あるいは溶媒を除去して作製されるが、その方法は通常の方法でよく、加熱、減圧あるいはその組合せで行われるのが一般的である。しかし、均一な高分子マトリクスフィルムを作製するには、高分子微粒子成分のガラス転移温度以上に加熱するのが好適である。また、必要に応じて加圧プレスして、高分子マトリクスを任意の形状に成形することも可能である。分散媒体の水あるいは溶媒が、固体電解質適用先の電池等に悪影響を与えるときには、この分散媒体の沸点以上に加熱するか、加熱と減圧処理を組合せて、分散媒体を取除かなければならない。

【0015】電解液の含浸は通常の方法でよく、例えば高分子微粒子分散液から作製した高分子マトリクスフィルムを電解液中に浸漬すればよい。電解液の含浸量は、浸漬時の温度と、浸漬時間の長さで制御できるが、高分子電解質中10重量%以上含浸させることが好適である。またあらかじめ、高分子微粒子分散液中に金属塩を

溶解させた場合は、極性溶媒、水又は両者の混合物を通常の方法で含浸させればよく、例えば、作製した高分子マトリクスを極性溶媒、水又は両者の混合物に浸漬させればよい。極性溶媒、水又は両者の混合物の含浸量は浸漬時の温度、並びに浸漬時間の長さで制御できるが、高分子電解質中10重量%以上含浸させることが好適である。

【0016】一方、本発明の全固体二次電池に用いられる正極シートは、高分子固体電解質が正極活物質へのイオン輸送の役割を担っている。この高分子固体電解質は、高いイオン伝導率を有する金属塩電解液がイオン伝導路となるため、正極シート中のイオンの拡散が速く、更に電解液が正極活物質と高分子固体電解質との界面にしみ出して、界面の接触抵抗を引下げる働きを持っている。このため、電池を構成した際の正極活物質の利用効率並びに比容量の増大が期待できる。更に、プロセスが単純なため、低い製造コストが期待できる。

【0017】正極シートに用いる正極活物質には、例えば V_2O_5 、 MnO_2 、 TiS_2 、 V_6O_{13} 、 Cr_2O_3 、 MoS_2 、 MoS_3 、 $NbSe$ あるいはこれらの混合物等が、また電子伝導性物質には熱分解黒鉛やアセチレンブラックあるいはこれらの混合物等が、それぞれ好適に用いられる。

【0018】正極シート中の高分子固体電解質に使用する高分子微粒子、安定剤及び電解液を構成する金属塩、溶媒は前述した高分子固体電解質で用いたものと同様なものでよい。また高分子微粒子分散液の製造方法も前記高分子固体電解質の製造方法と同様でよい。

【0019】高分子微粒子分散液中に電池正極活物質微粒子及び電子伝導体を分散させる方法は通常の方法でよく、電池正極活物質微粒子及び電子伝導体を高分子微粒子分散液に入れて、かくはんすればよい。この混合分散液中の電池正極活物質、電子伝導体、高分子微粒子の重量混合比を、それぞれ x 、 y 、 z とするとき、 $x+y+z=1$ かつ $0.3 \leq x \leq 0.8$ 、 $0.05 \leq y \leq 0.2$ 、 $0.2 \leq z \leq 0.6$ であることが好適である。

【0020】電池正極活物質微粒子及び電子伝導体を含む上記高分子微粒子分散液から、水、極性溶媒又は両者の混合物を除去する方法は通常の方法でよく、例えば加熱、減圧あるいはその組合せで蒸発させればよい。このプロセスにより、分散していた高分子微粒子はお互いに融着し高分子マトリクスが形成され、電池正極活物質微粒子、電子伝導体のバインダーとなり、本発明の電池正極シートの前駆構造が作製される。作製は、高分子マトリクスのガラス転移温度以上かつ正極活物質が分解しない温度領域で行う必要がある。また必要に応じて加圧プレスして、シートを任意の形状に成形することも可能である。分散媒体の水あるいは溶媒が、固体電解質適用先の電池等に悪影響を与えるときには、この分散媒体の沸点以上に加熱するか、加熱と減圧を組合せて、分散

媒体を取除かなければならない。

【0021】電解液の含浸は通常の方法でよく、例えば作製した正極シート前駆構造を電解液中に浸漬すればよい。電解液の含浸量は浸漬時の温度、並びに浸漬時間の長さで制御できるが、高分子電解質成分に対して10重量%以上含浸させることが好適である。また、あらかじめ高分子微粒子分散液中に金属塩を溶解させた場合は、極性溶媒、水又は両者の混合物を通常の方法で含浸させればよく、例えば作製した正極シート前駆構造を極性溶媒、水又は両者の混合物の中に浸漬すればよい。極性溶媒、水又は両者の混合物の含浸量は浸漬時の温度、並びに浸漬時間の長さで制御できるが、高分子マトリクス成分に対して10重量%以上含浸させることが好適である。

【0022】本発明の全固体二次電池は、前記負極、前記高分子固体電解質、前記正極をこの順に積層することにより作製される。該電池を構成するその他の構造材料は従来公知のものでよい。

【0023】

【実施例】以下、本発明を実施例により更に具体的に説明するが、本発明はこれら実施例に限定されない。

【0024】実施例1

高分子固体電解質の作製： 高分子微粒子分散液として、界面活性剤を含む日本ゼオン社製スチレン・ブタジエン系ラテックス（商品名：Nipol LX206）10g をとり、常圧、95℃で加熱し、固形分が70重量%になるまで乾燥した後、塗布厚さ100μmのフィルムアプリケータでシート状に引延ばした。更に100℃で1時間乾燥した後、水中に浸漬し、入念に洗浄した。洗浄終了後、常温で3時間、100℃で3時間真空乾燥させ、高分子マトリクスフィルムを得た。次に過塩素酸リチウムのプロピレンカーボネート溶液（濃度1 mol/l）を調製し、ここで作製した高分子マトリクスフィルムを24時間浸漬して（50℃）電解液を含浸させ、高分子固体電解質を得た。また、得られた高分子固体電解質フィルムは十分な機械的強度を有していた。

正極シートの作製： 界面活性剤を含んだ、高分子微粒子分散液〔日本ゼオン社製スチレン・ブタジエン系ラテックス（商品名：Nipol LX206）〕10g中に五酸化二バナジウム（関東化学社製）3g、並びにアセチレンブラック（電気化学工業社製）0.6gを分散させた。70℃の温度下、分散液中の固形分が約70%になるまで乾燥させた後、この分散液を塗布厚さ100μmのフィルムアプリケータでシート状に引延ばした。常温で24時間、60℃で10時間真空乾燥させ、正極シート前駆構造を得た。次に、過塩素酸リチウムのプロピレンカーボネート溶液（濃度1 mol/l）を調製し、ここに上記シートを50℃の温度条件下、浸漬し、正極シートを得た。得られた正極シートは、十分な機械的強度を有しかつ柔軟性のあるシートであり、含浸された電解液

は、本シートを加圧してもしみ出すことはなかった。次に、リチウム金属箔（厚さ70 μ m）、前記高分子固体電解質（厚さ30 μ m）及び前記正極シート（厚さ93 μ m）をこの順に積層し、これをコインセルケース内に封入した。上記電池作製の全行程はアルゴン雰囲気グローブボックス内で行った。この電池を電圧範囲3.5～1.8V、放電電流1mA、充電電流1mAの条件で充放電試験を行った結果、比容量178mAh/gが得られた。

【0025】実施例2

高分子固体電解質の作製： 高分子微粒子分散液として、界面活性剤を含む日本ゼオン社製スチレン・ブタジエン系ラテックス（商品名：Nipol LX206）10g中に過塩素酸リチウム0.07gを溶解させ、常圧、95℃で加熱し、固形分が70重量%になるまで乾燥させた。その後、この高分子微粒子分散液を塗布厚さ100 μ mのフィルムアブリケータでシート状に引延ばし、常温で3時間、100℃で3時間真空乾燥させ、高分子マトリクスフィルムを得た。次に、ここに作製した高分子マトリクスフィルムをプロピレンカーボネートの中に、

24時間浸漬させ（50℃）、高分子固体電解質を得た。また、得られた高分子固体電解質フィルムは十分な機械的強度を有していた。

正極シートの作製： 界面活性剤を含んだ、高分子微粒子分散液〔日本ゼオン社製スチレン・ブタジエン系ラテックス（商品名：Nipol LX206）10g中に五酸化*

*ニバナジウム（関東化学社製）3g、並びにアセチレンブラック（電気化学工業社製）0.6gを分散させた。分散液中に過塩素酸リチウム0.07gを溶解させ、70℃の温度下、分散液中の固形分が約70%になるまで乾燥させた後、この分散液を塗布厚さ100 μ mのフィルムアブリケータでシート状に引延ばした。常温で24時間、60℃で10時間真空乾燥させ、正極シート前駆構造を得た。次に、プロピレンカーボネート中に上記シートを50℃で浸漬し、正極シートを得た。得られた正極シートは、十分な機械的強度を有しかつ柔軟性のあるシートであり、含浸された電解液は、本シートを加圧してもしみ出すことはなかった。次に、リチウム金属箔（厚さ70 μ m）、前記高分子固体電解質（厚さ34 μ m）及び前記正極シート（厚さ90 μ m）をこの順に積層し、これをコインセルケース内に封入した。上記電池作製の全行程はアルゴン雰囲気グローブボックス内で行った。この電池を電圧範囲3.5～1.8V、放電電流1mA、充電電流1mAの条件で充放電試験を行った結果、比容量180mAh/gが得られた。

【0026】

【発明の効果】以上の説明で明らかなように、本発明の全固体二次電池は、高電圧、大容量でかつ充放電特性、安全性に優れるという特徴を有しており、リチウム固体二次電池等の全固体二次電池の特性向上を達成できる利点がある。

フロントページの続き

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CLAIMS

[Claim(s)]

[Claim 1] In a negative electrode, a solid polymer electrolyte, and all the solid-state rechargeable batteries that consist of a positive electrode the aforementioned solid polymer electrolyte A macromolecule matrix and the metal salt electrolytic solution are made into a principal component. Water, a polar solvent, or a macromolecule meltable into both mixture, The metal salt electrolytic solution carries out phase separation to a macromolecule matrix including the mixture of a surfactant or both. The mixture of the aforementioned water, a polar solvent or a macromolecule meltable into both mixture, a surfactant, or both is stabilizing mutual distribution of a macromolecule matrix and the metal salt electrolytic solution, And all the solid-state rechargeable batteries characterized by being the positive-electrode sheet with which the aforementioned positive electrode distributed the cell positive-active-material particle and the electronic-conduction object in this polyelectrolyte.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] Especially this invention relates to high-energy density solid-state rechargeable batteries, such as a lithium solid-state rechargeable battery. It is related with the high voltage and all the solid-state rechargeable batteries that are large capacity and were excellent in a charge-and-discharge property and safety in detail.

[0002]

[Description of the Prior Art] In recent years, the needs of a cell which have high-energy density are increasing as a power supply for small and pocket electronic equipment. As a typical thing of the cell which fills such needs, the cell using alkali metal, especially the lithium is mentioned to a negative electrode. Since the organic electrolytic solution which dissolved lithium salt in the electrolyte is used for the lithium cell, it cannot say now that a liquid spill, dendrite short-circuit, etc. have the enough reliability in a safety aspect. For this reason, realization of the cell of all solid-state types which used the solid electrolyte made in the inorganic substance or the macromolecule is expected. Examination is briskly advanced in recent years from that the mass cell with easy large-area-izing for the solid state battery constituted by the electrolyte using the positive-electrode sheet which uses as a binder the solid polymer electrolyte which has ion conductivity in a solid polymer electrolyte in a positive electrode again especially can be realized, or the producing method being comparatively simple. conventionally, although the system which dissolved the metal salt into polyether compounds, such as a polyethylene oxide (PEO), has been briskly studied by such solid polymer electrolyte, to it, the ionic conductivity of 10 to 4 or more S/cm is discovered in Watanabe, Ogata, surface-of-metal technology, the 37th volume, No. 5, [the 214th - refer to the 221 page (1986)], and near a room temperature — things were impossible Although the electrolytic-solution sinking-in type solid polymer electrolyte which infiltrated the metal salt electrolytic solution into the polar macromolecule captures the spotlight and journal OBU power [besides for example, a cox van (Koksang)] SOSESU (Journal of Power Sources), the 32nd volume, [the 175th - referring to the 185 page (1990)], and its ionic conductivity have arrived at the 10-3 S/cm base in recent years again It had the trouble in a manufacturing process, such as passing through the process which cost requires in risk, such as radiation irradiation. The example which, on the other hand, used for the binder the solid polymer electrolyte which dissolved the metal salt in PEO as an example of research of the conventional positive-electrode sheet (although there are solid State ionics (Solid State Ionics) besides for example, M.Z.A. MUNSHI (M. Z.A.Munshi), the 41st volume, and 41-46th page (1988))] Above 60 degrees C which PEO softens, although the good property was shown, in near a room temperature, the ionic diffusion in a positive-electrode sheet was late, and contact of the interface of a positive active material and a solid polymer electrolyte had further the fault that it was bad and the utilization factor of a positive electrode became low.

[0003]

[Problem(s) to be Solved by the Invention] this invention is made in view of such the present condition, and the purpose is in offering the high voltage and all the solid-state rechargeable batteries that are large capacity and were excellent in a charge-and-discharge property and safety.

[0004]

[Means for Solving the Problem] If this invention is outlined, it will be invention about a negative electrode, a solid polymer electrolyte, and all the solid-state rechargeable batteries that consist of a positive electrode. The aforementioned solid polymer electrolyte makes a principal component a macromolecule matrix and the metal salt electrolytic solution. It is what contains the mixture of a meltable macromolecule, a surfactant, or both in the mixture of water, a polar solvent, or both. And the thing for which the metal salt electrolytic solution carries out phase separation to a macromolecule matrix, and the mixture of a meltable macromolecule, a surfactant, or both is stabilizing mutual distribution of a macromolecule matrix and the metal salt electrolytic solution into the mixture of the aforementioned water, a polar solvent, or both, And the aforementioned positive electrode is characterized by being the positive-electrode sheet which distributed the cell positive-active-material particle and the electronic-conduction object in this polyelectrolyte.

[0005] When the negative electrode used for the solid-state rechargeable battery of this invention considers application to a lithium secondary battery, low voltage intercalation compounds, such as a lithium metallic foil, a lithium-aluminium alloy, or lithium-carbon, are used suitably.

[0006] The ionic conduction way which consists of the metal salt electrolytic solution is formed into the matrix film with which the solid polymer electrolyte used for the solid-state rechargeable battery of this invention was produced from macromolecule particle dispersion liquid. As for this solid polymer electrolyte, the condensation portion of the polar stabilizer in a macromolecule matrix (a macromolecule meltable on a dispersion-medium object, a surfactant, or both mixture) infiltrates the electrolytic solution, and it can be manufactured. Or a metal salt is beforehand dissolved in macromolecule particle dispersion liquid, after forming a macromolecule matrix, the mixture of the polar solvent and water which dissolve a metal salt in the condensation portions of the polar stabilizer in the produced macromolecule matrix film and a metal salt, or both can be infiltrated, and the ionic conduction way which consists of the electrolytic solution which dissolved the metal salt can be formed again. In these solid polymer electrolytes, since the electrolytic solution is carrying out phase separation from the macromolecule matrix, prevention of ionic migration in case an interaction with electrostatic electrolytic solution and macromolecule matrix is in a macromolecule matrix unlike the conventional electrolytic-solution sinking-in type solid polymer electrolyte which the electrolytic solution is distributing on molecule level is suppressed, and the ionic conduction way of high ion conductivity is stably obtained also to long-term use.

[0007] Moreover, in order to carry out phase separation to the polar electrolytic solution, a hydrocarbon system macromolecule with cheap required a macromolecule matrix having low polarity or its copolymer is used suitably. Furthermore, as for this solid polymer electrolyte, a manufacture process can expect eye a simple hatchet and a low manufacturing cost.

[0008] Although what thing may be used as long as the macromolecule component when forming a macromolecule matrix carries out phase separation to the electrolytic solution as a component of the macromolecule particle used when manufacturing this solid polymer electrolyte, that to which polarity uses a low macromolecule, for example, a cheap hydrocarbon system macromolecule, or its copolymer as a component is suitable. As a macromolecule component in a macromolecule particle, it is independent or a copolymer containing polystyrene to which mixture is mentioned, polypropylene, the poly isobutene, polyethylene, a polybutadiene, a polyisoprene, poly (alpha methyl styrene), poly butyl methacrylate, poly butyl acrylate, poly (2-ethylhexyl acrylate), the poly dibutyl phthalate, a polyvinyl butyl ether, a polyvinyl butyral, polyvinyl formals, and these components of the following etc., for example. Mixture of two or more sorts of particles which have a different component also about a macromolecule particle is sufficient. As for the particle size of the macromolecule particle of a particle, a 0.01-50-micrometer thing is used suitably.

[0009] Independent or mixture, such as fatty-acid metal salt with which a surfactant is suitably used for the stabilizer of macromolecule particle dispersion liquid, for example, the following is mentioned to it, an alkylbenzene sulfonic-acid metal salt, an alkyl-sulfuric-acid metal salt, a dioctyl sulfosuccinate metal salt, the polyoxyethylene nonylphenyl ether, polyoxyethylene stearic acid ester, polyoxyethylene sorbitan monochrome lauric-acid ester, a polyoxyethylene-polyoxypropylene block copolymer, and a polyether denaturation silicone oil.

[0010] Moreover, the macromolecule which can dissolve in a dispersion-medium object as a stabilizer may be used, and a macromolecule particle may be distributed. As such a macromolecule, although it changes with dispersion-medium objects, when water is a dispersion-medium object, a hydroxyethyl cellulose, polyvinyl alcohol, a polyacrylic-acid metal salt, a methyl cellulose, etc. are mentioned. Although water is suitably used for the dispersion-medium object of macromolecule particle dispersion liquid, polar organic solvents, such as alcohols, can be used.

[0011] Although the metal salt which is the component of the electrolytic solution used as an ionic conduction way changes with uses of the polyelectrolyte to produce When application to a lithium cell is considered as an example, LiClO_4 and LiAlCl_4 , Lithium salt and such mixture, such as LiBF_4 , LiPF_6 , LiAsF_6 , LiNbF_6 , LiSCN , LiCl , and $\text{Li}(\text{CF}_3\text{SO}_3)$, $\text{Li}(\text{C}_6\text{H}_5\text{SO}_3)$, are mentioned as an example.

[0012] Moreover, if application to a lithium cell is similarly assumed as an example, non-proton nature polar solvents and such mixture, such as propylene carbonate, ethylene carbonate, gamma-butyrolactone, dimethyl carbonate, dimethyl sulfoxide, an acetonitrile, a sulfolane, a dimethylformamide, a dimethylacetamide, 1, 2-diethoxy ethane, 1, 2-dimethoxyethane, a tetrahydrofuran, 2-methyl tetrahydrofuran, a dioxolane, and methyl acetate, will be mentioned to the solvent of the electrolytic solution as an example. The mixing ratio of the above-mentioned metal salt and a solvent is the ionic conduction way formed into the solid polymer electrolyte, and it is suitable for it to prepare so that metal salt concentration may serve as 0.01 - 5 mol/l.

[0013] although macromolecule particle dispersion liquid can develop and distribute a polymer solution in a distributed solvent, and can be atomized, a surfactant or a dispersion-medium object can be made to be able to use and stabilize the macromolecule of fusibility and it can manufacture — a drainage system dispersion medium — it is suitable to manufacture by the emulsion-polymerization method in a body Moreover, macromolecule particle dispersion liquid can also be manufactured by the distributed polymerization among polar solvents, such as alcohol, [refer to a British polymer journal (British PolymerJournal) besides [for example,] Y. ARUMOGU (Y. Almog), the 14th volume, and the 131st page (1982)]. Generally the process of the macromolecule dispersion liquid by the emulsion-polymerization method is known well, and is often outlined to [for example, Soichi Muroi work, macromolecule latex admission (1st ** of the first edition) (**** Co., July 29, Showa 55 issue) reference], and the following. If a surfactant is underwater added more than critical micelle concentration and a monomer is introduced, a part

of monomer will be incorporated inside a surfactant micell. If a water-soluble polymerization initiator is added and heated, a polymerization initiator radical will occur, if it enters into the micell which swelled in the monomer, a monomer will carry out a polymerization and a macromolecule will be compounded. While a macromolecule particle grows by polymerization reaction, a monomer is supplied to the micell of a reaction place through the underwater dissolution from the emulsified monomer drop. The path of a macromolecule particle is controllable by adjusting reaction time.

[0014] Although the macromolecule matrix film of a solid polymer electrolyte removes water or a solvent from macromolecule particle dispersion liquid and is produced, the usual method is sufficient as the method, and it is common to be carried out in heating, reduced pressure, or its combination. However, in order to produce a uniform macromolecule matrix film, it is suitable to heat more than the glass transition temperature of a macromolecule particle component. Moreover, it is also possible to carry out a pressurization press if needed and to fabricate a macromolecule matrix in arbitrary configurations. When the water or the solvent of a dispersion-medium object has a bad influence on the cell of a solid electrolyte application place etc., it must heat more than the boiling point of this dispersion-medium object, or must remove a dispersion-medium object combining heating and reduced pressure processing.

[0015] Sinking [of the electrolytic solution] in should just be immersed into the electrolytic solution in the macromolecule matrix film which the usual method is sufficient as, for example, was produced from macromolecule particle dispersion liquid. Although the amount of sinking in of the electrolytic solution is controllable by the temperature at the time of being immersed, and the length of immersing time, it is suitable for it to make it sink in 10% of the weight or more among a polyelectrolyte. Moreover, what is necessary is just to make the produced macromolecule matrix beforehand immersed in the mixture of a polar solvent, water, or both that what is necessary is just to infiltrate the mixture of a polar solvent, water, or both by the usual method, when a metal salt is dissolved into macromolecule particle dispersion liquid. Although a polar solvent, water, or the amount of sinking in of both mixture is controllable by the temperature at the time of being immersed, and the length of immersing time, it is suitable to make it sink in 10% of the weight or more among a polyelectrolyte.

[0016] On the other hand, as for the positive-electrode sheet used for all the solid-state rechargeable batteries of this invention, the solid polymer electrolyte is playing a role of the ion transport to a positive active material. Since the metal salt electrolytic solution which has ionic conductivity with this high solid polymer electrolyte serves as an ionic conduction way, diffusion of the ion in a positive-electrode sheet is quick, and it has further the work to which the electrolytic solution oozes out to the interface of a positive active material and a solid polymer electrolyte, and reduces the contact resistance of an interface. For this reason, increase of the utilization factor of the positive active material at the time of constituting a cell and the amount of specific volume is expectable. Furthermore, a process can expect eye a simple hatchet and a low manufacturing cost.

[0017] V2 O5, MnO2, TiS2, V6 O13, Cr3 O8, MoS2, MoS3, NbSe(s), or such mixture are used for the positive active material used for a positive-electrode sheet, and a pyrolytic graphite, acetylene black, or such mixture are suitably used for the electronic-conduction nature matter, respectively.

[0018] The metal salt which constitutes the macromolecule particle, the stabilizer, and the electrolytic solution which are used for the solid polymer electrolyte in a positive-electrode sheet, and a solvent are easy to be the same as that of what was used by the solid polymer electrolyte mentioned above. Moreover, the manufacture method of macromolecule particle dispersion liquid is the same as the manufacture method of the aforementioned solid polymer electrolyte, and is good.

[0019] The usual method is sufficient as the method of distributing a cell positive-active-material particle and an electronic-conduction object in macromolecule particle dispersion liquid, a cell positive-active-material particle and an electronic-conduction object are put in into macromolecule particle dispersion liquid, and it should just agitate them. the weight of the cell positive active material in these mixed dispersion liquid, an electronic-conduction object, and a macromolecule particle — when setting a mixing ratio to x, and y and z, respectively, it is suitable that it is $x+y+z=1$ and $0.3 \leq x \leq 0.8$, $0.05 \leq y \leq 0.2$, and $0.2 \leq z \leq 0.6$

[0020] What is necessary is for the usual method to be sufficient as the method of removing the mixture of water, a polar solvent, or both, for example, just to evaporate it in heating, reduced pressure, or its combination from the above-mentioned macromolecule particle dispersion liquid containing a cell positive-active-material particle and an electronic-conduction object. According to this process, the dispersed macromolecule particle is welded to each other, a macromolecule matrix is formed, it becomes the binder of a cell positive-active-material particle and an electronic-conduction object, and the precursive structure of the cell positive-electrode sheet of this invention is produced. It is necessary to perform production in the temperature field which more than the glass transition temperature of a macromolecule matrix and a positive active material do not decompose. Moreover, it is also possible to carry out a pressurization press if needed and to fabricate a sheet in arbitrary configurations. When the water or the solvent of a dispersion-medium object has a bad influence on the cell of a solid electrolyte application place etc., it must heat more than the boiling point of this dispersion-medium object, or must remove a dispersion-medium object combining heating and reduced pressure.

[0021] Sinking [of the electrolytic solution] in should just be immersed into the electrolytic solution in the positive-electrode sheet precursive structure which the usual method is sufficient as, for example, was

produced. Although the amount of sinking in of the electrolytic solution is controllable by the temperature at the time of being immersed, and the length of immersing time, it is suitable to make it sink in 10% of the weight or more to a polyelectrolyte component. Moreover, what is necessary is just to immerse the produced positive-electrode sheet precursive structure into the mixture of a polar solvent, water, or both that what is necessary is just to infiltrate the mixture of a polar solvent, water, or both by the usual method, when a metal salt is beforehand dissolved into macromolecule particle dispersion liquid. Although a polar solvent, water, or the amount of sinking in of both mixture is controllable by the temperature at the time of being immersed, and the length of immersing time, it is suitable to make it sink in 10% of the weight or more to a macromolecule matrix component.

[0022] All the solid-state rechargeable batteries of this invention are produced by carrying out the laminating of the aforementioned negative electrode, the aforementioned solid polymer electrolyte, and the aforementioned positive electrode to this order. It is easy to be well-known [the structural material of others which constitute this cell] conventionally.

[0023]

[Example] Hereafter, although an example explains this invention still more concretely, this invention is not limited to these examples.

[0024] Production of example 1 solid polymer electrolyte: As macromolecule particle dispersion liquid, styrene butadiene system latex (tradename : Nipol LX206) by Nippon Zeon Co., Ltd. 10g containing a surfactant was taken, and it heated at an ordinary pressure and 95 degrees C, and after drying until the solid content became 70% of the weight, it extended in the shape of a sheet by the film applicator with an application thickness of 100 micrometers. After drying at 100 more degrees C for 1 hour, it was immersed underwater and washed carefully. After the washing end, the vacuum drying was carried out at 100 degrees C with ordinary temperature for 3 hours for 3 hours, and the macromolecule matrix film was obtained. Next, the propylene carbonate solution (concentration 1 mol/l) of a lithium perchlorate was prepared, the macromolecule matrix film produced here was immersed for 24 hours, the electrolytic solution (50 degrees C) was infiltrated, and the solid polymer electrolyte was obtained. Moreover, the obtained solid-polymer-electrolyte film had sufficient mechanical strength.

Production of a positive-electrode sheet: 5 oxidation 2 vanadium (Kanto chemistry company make) 3g and acetylene black (DENKI KAGAKU KOGYO K.K. make) 0.6g were distributed in macromolecule particle dispersion-liquid [styrene [by Nippon Zeon Co., Ltd.]-butadiene system latex (tradename : Nipol LX206)] 10g containing the surfactant. After making it dry until the solid content under the temperature of 70 degrees C and in dispersion liquid became about 70%, these dispersion liquid were extended in the shape of a sheet by the film applicator with an application thickness of 100 micrometers. The vacuum drying was carried out at 60 degrees C with ordinary temperature for 10 hours for 24 hours, and positive-electrode sheet precursive structure was acquired. Next, the propylene carbonate solution (concentration 1 mol/l) of a lithium perchlorate was prepared, the above-mentioned sheet was immersed under the 50-degree C temperature condition, and the positive-electrode sheet was obtained here. The obtained positive-electrode sheet was a sheet which has sufficient mechanical strength and is supple, and even if the electrolytic solution into which it sank pressurized this sheet, it did not ooze out. Next, the laminating of a lithium metallic foil (70 micrometers in thickness), the aforementioned solid polymer electrolyte (30 micrometers in thickness), and the aforementioned positive-electrode sheet (93 micrometers in thickness) was carried out to this order, and this was enclosed in the coin cell case. The stroke of the above-mentioned cell production was performed within the glove box of argon atmosphere. In this cell, as a result of performing a charge and discharge test on the conditions of the voltage ranges 3.5-1.8V, 1mA of discharge currents, and 1mA of charging currents, amount of specific volume 178 mAh/g was obtained.

[0025] production of example 2 solid polymer electrolyte: styrene butadiene system latex (tradename : Nipol LX206) by Nippon Zeon Co., Ltd. 10g which contains a surfactant as macromolecule particle dispersion liquid — 0.07g of lithium perchlorates is dissolved in inside, and it heats at an ordinary pressure and 95 degrees C, and it was made to dry until a solid content became 70% of the weight. Then, these macromolecule particle dispersion liquid were extended in the shape of a sheet by the film applicator with an application thickness of 100 micrometers, the vacuum drying was carried out at 100 degrees C with ordinary temperature for 3 hours for 3 hours, and the macromolecule matrix film was obtained. Next, the macromolecule matrix film produced here was made immersed into propylene carbonate for 24 hours (50 degrees C), and the solid polymer electrolyte was obtained. Moreover, the obtained solid-polymer-electrolyte film had sufficient mechanical strength.

production of a positive-electrode sheet: styrene [by macromolecule particle dispersion-liquid [Nippon Zeon Co., Ltd.]-butadiene system latex (tradename : Nipol LX206) 10g containing the surfactant — 5 oxidation 2 vanadium (Kanto chemistry company make) 3g and acetylene black (DENKI KAGAKU KOGYO K.K. make) 0.6g were distributed to inside 0.07g of lithium perchlorates was dissolved into dispersion liquid, and after making it dry until the solid content under the temperature of 70 degrees C and in dispersion liquid became about 70%, these dispersion liquid were extended in the shape of a sheet by the film applicator with an application thickness of 100 micrometers. The vacuum drying was carried out at 60 degrees C with ordinary temperature for 10 hours for 24 hours, and positive-electrode sheet precursive structure was acquired. Next, the above-mentioned sheet was immersed at 50 degrees C into propylene carbonate, and the positive-electrode sheet was obtained. The obtained positive-electrode sheet was a sheet which has

sufficient mechanical strength and is supple, and even if the electrolytic solution into which it sank pressurized this sheet, it did not ooze out. Next, the laminating of a lithium metallic foil (70 micrometers in thickness), the aforementioned solid polymer electrolyte (34 micrometers in thickness), and the aforementioned positive-electrode sheet (90 micrometers in thickness) was carried out to this order, and this was enclosed in the coin cell case. The stroke of the above-mentioned cell production was performed within the glove box of argon atmosphere. In this cell, as a result of performing a charge and discharge test on the conditions of the voltage ranges 3.5-1.8V, 1mA of discharge currents, and 1mA of charging currents, amount of specific volume 180 mAh/g was obtained.

[0026]

[Effect of the Invention] In the above explanation, all the solid-state rechargeable batteries of this invention are a high voltage and large capacity so that clearly, and it has the feature of excelling in a charge-and-discharge property and safety, and there is an advantage which can attain the improvement in a property of all solid-state rechargeable batteries, such as a lithium solid-state rechargeable battery.

[Translation done.]

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*English abstract
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(54) ALL-SOLID SECONDARY BATTERY

(57)Abstract:

PURPOSE: To provide an all-solid secondary battery which works with a high voltage presents a large capacity and charge/discharge characteristics, and excels in the safety.

CONSTITUTION: An all-solid secondary battery is composed of a neg. electrode, highpolymer solid electrolyte, and pos. electrode, wherein the solid electrolyte contains chiefly a highpolymer matrix and a metal salt electrolytic solution and also contains highpolymer and/or surface active agent which are soluble in water and/or polar solvent. Therein the matrix and the electrolytic solution are phase segregated, and the highpolymer and/or surface active agent stabilize co-dispersion of the matrix and electrolytic solution. The pos. electrode assumes a sheet form in which pos. electrode active substance particulates and electron conductor are dispersed in the highpolymer solid electrolyte. Thereby the characteristics of all-solid secondary battery can be enhanced.

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